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## EFFECT OF PHOSPHORUS OXIDE ADDITIONS ON THE SPECTRAL-OPTICAL CHARACTERISTICS OF SILICATE GLASSES

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The effect of small phosphorus oxide additions on the optical transmission of silicate glasses in the visible and near-IR regions is studied. It is shown that an increase of the phosphorus concentration is accompanied by an intensification of IR absorption; this is due to an increase of the relative content of divalent iron and its possible transition to octahedral coordination. The increase of visible-range absorption is negligible and cannot become an obstacle for phosphorus doping of commercial silicate glasses.

**Key words:** silicate glass, additions, phosphorus oxide, spectral-optical characteristics.

Small phosphorus oxide additions have a positive effect on the technological and usage properties of commercial silicate glasses [1–3]. The influence of these additions on the spectral–optical properties of glasses, first and foremost, sheet glass, for which the importance of these properties is paramount, is certainly of interest.

Phosphorus oxide additions could be responsible for the formation of liquation and crystalline micro-non-uniformities. In addition, phosphorus oxide increases the relative content of divalent iron [4], which could affect the spectral properties of glasses.

Phosphorus, which is found in silicate glasses in the form of the tetrahedra  $[\text{P}_4]^{+}$ , has the maximum degree of oxidation +5 and cannot be a reducing agent or an oxidizer, i.e., it has no effect on the oxidation–reduction equilibrium in glass-forming silicate melt. Therefore, in the opinion of the authors of [5] the elemental composition of glass and the structural position of the iron ions, which depends on the nature of the main glass formers —  $\text{Si}^{4+}$  and  $\text{P}^{5+}$ , affects the valence equilibrium  $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$  in this case.

Opinions differ in respect to the structure–coordination position of iron in silicate glasses. Most investigators are of the opinion that  $\text{Fe}^{3+}$  ions can be found in tetrahedral coordination and participate in the formation of the structural framework as well as in octahedral coordination and function as modifiers; this is determined by, first and foremost, the concentration of the alkali oxides. For the  $\text{Fe}^{2+}$  ions, because of the large ionic radius and small charge, octahedral coordi-

nation and the modifier role are more likely. However, some authors, specifically, the authors of [5], are of the opinion that finding  $\text{Fe}^{2+}$  ions in tetrahedral coordination in silicate glasses and acting as a network former are entirely likely for a definite ratio of the components.

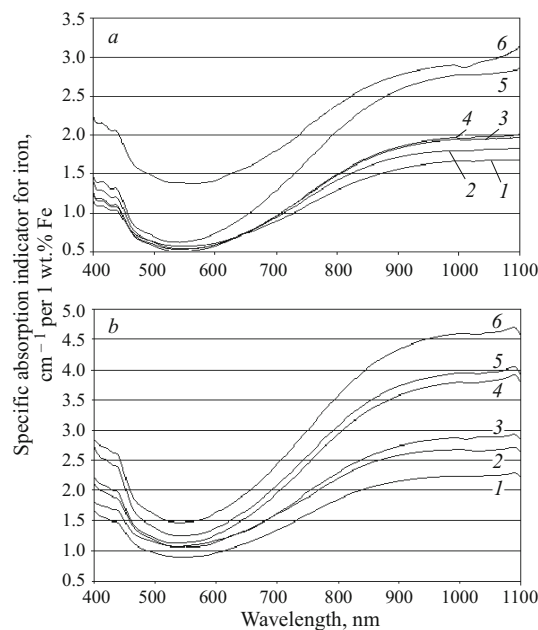
In the present work we studied the effect of phosphorus oxide additions on the optical transmission of glass in the visible and near-IR ranges of the spectrum. For these investigations we synthesized model glasses of the series  $\text{LF}_1$  and  $\text{LF}_2$  with variable  $\text{P}_2\text{O}_5$  content; this component was introduced in amounts 0–0.9% (molar content) as a substitute for  $\text{SiO}_2$ . On the whole the glass compositions are close to the composition of commercial float glass. Iron had to be introduced in elevated concentrations in order to obtain more distinct and stable dependences. The chemical composition of the model glasses is presented in Table 1.

The molar content of the oxides in the model glasses was as follows (%): 69.7–70.8  $\text{SiO}_2$ , 1.0  $\text{Al}_2\text{O}_3$ , 9.0  $\text{CaO}$ , 6.0  $\text{MgO}$ , 13.0  $\text{Na}_2\text{O}$ , 0–0.9  $\text{P}_2\text{O}_5$ , and 0.2–0.3  $\text{Fe}_2\text{O}_3$ .

Chemically pure and analytically pure reactive initial materials were used to synthesize the model glasses. Iron was introduced in the form of oxalate  $\text{Fe}(\text{II})$ . The glass was made in a Silit electric furnace at 1400°C and cast into plates, which were annealed in a muffle furnace at 550°C. None of the glasses contained inclusions of incomplete melting; the glasses were all homogeneous and x-ray amorphous. Plane-parallel plates were made from glass samples to determine the optical transmission; the plates were scanned in a SF-56 spectrophotometer in the wavelength range 400–1100 nm.

The spectral curves of the specific absorption indicators for iron in the model glasses are displayed in Fig. 1.

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**Fig. 1.** Spectral curves of the specific absorption indicators of iron in LF<sub>1</sub> (a) and LF<sub>2</sub> (b) series glasses. The numbers on the curves correspond to the compositions with same number in Table 1.

The specific absorption indicator for iron  $\chi_{\lambda, \text{Fe}}$  (cm<sup>-1</sup> per 1 wt.% Fe) was calculated from the relation [6]:

$$\chi_{\lambda, \text{Fe}} = \frac{-\log \tau_{\lambda} - 2D_{pm}}{lm_{\text{Fe}(\text{tot})}},$$

where  $\tau_{\lambda}$  is the transmission of the glass sample at the wavelength  $\lambda$ , arb. units;  $D_{pm}$  is the correction for multiple reflection and is neglected in the calculations because it is small;  $l$  is the thickness of the glass sample, cm; and,  $m_{\text{Fe}(\text{tot})}$  is the mass content of iron in terms of the metal, %.

**TABLE 1.**

Glass	Content, wt. %						
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	Fe <sub>2</sub> O <sub>3</sub>
LF <sub>1</sub> -1	71.61	1.72	8.50	4.05	13.59	0.00	0.54
LF <sub>1</sub> -2	71.41	1.72	8.48	4.04	13.57	0.24	0.54
LF <sub>1</sub> -3	71.21	1.71	8.47	4.03	13.55	0.48	0.54
LF <sub>1</sub> -4	71.01	1.71	8.46	4.03	13.53	0.72	0.54
LF <sub>1</sub> -5	70.42	1.71	8.43	4.01	13.48	1.42	0.54
LF <sub>1</sub> -6	69.83	1.70	8.39	4.00	13.42	2.13	0.53
LF <sub>2</sub> -1	71.41	1.72	8.50	4.05	13.59	0.00	0.74
LF <sub>2</sub> -2	71.21	1.72	8.48	4.04	13.57	0.24	0.74
LF <sub>2</sub> -3	71.01	1.71	8.47	4.03	13.55	0.48	0.74
LF <sub>2</sub> -4	69.81	1.71	8.46	4.03	13.53	0.72	0.74
LF <sub>2</sub> -5	70.22	1.71	8.43	4.01	13.48	1.42	0.74
LF <sub>2</sub> -6	69.63	1.70	8.39	4.00	13.42	2.13	0.73

Study of the spectral curves shows that as the P<sub>2</sub>O<sub>5</sub> content increases, the optical absorption in the long-wavelength range increases. As shown in [5], the transmission spectra of the silicate glasses made under normal and reducing conditions and containing di- and trivalent iron, are mainly represented by the characteristic absorption of the Fe<sup>2+</sup> ions, which dominates in the visible and IR regions with a maximum at about 1000 nm. The absorption by Fe<sup>3+</sup> is much weaker and is superposed on the absorption by Fe<sup>2+</sup>. For this reason, the increase of absorption observed in Fig. 1 at long wavelengths indicates that the relative content of divalent iron increases.

A substantial increase of IR absorption with a negligible change of absorption in the visible range can be seen in the series LF<sub>1</sub> glasses. This can be explained not only by an increase of the relative content of divalent iron but also by a possible change in its structural position and transition from tetra- to octahedral coordination, which increases IR absorption. For the LF<sub>1</sub>-6 composition, an increase of absorption is seen at all wavelengths, including in the visible range. This can be attributed to the formation of a heterogeneous structure and the appearance of liquation micro-non-uniformities, which scatter light strongly.

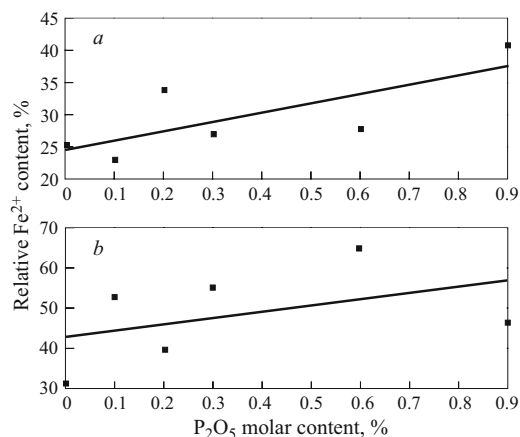
For series LF<sub>2</sub> glasses phosphorus oxide has a stronger effect on the optical absorption in the visible and IR ranges. Here, together with an increase of the relative of the divalent iron content it is possible that iron in this form transitions from tetrahedral to octahedral coordination. Judging from the spectral curves, the effect Here, together with an increase of the relative of the divalent iron content it is possible that iron in this form transitions from tetrahedral to octahedral coordination. of phosphorus oxide on the right-ward shift of the equilibrium  $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$  is greater for series LF<sub>2</sub> glasses, where the total iron content is greater.

Figure 2 displays the relative content of divalent iron in the model glasses versus the amount of P<sub>2</sub>O<sub>5</sub> (according to the spectrophotometric measurements). The calculation was performed according to the following relation using the method described in [6]:

$$d_{\text{Fe(II)}} = \frac{-\log \tau_{\lambda} - 2D_{pm}}{lm_{\text{Fe}(\text{tot})}\rho\varphi_{\lambda, \text{Fe(II)}}} \times 100,$$

where  $\tau_{\lambda}$  is the transmission of the glass sample at wavelength 800 or 1000 nm, arb. units;  $\rho$  is the density of the glass, g/cm<sup>3</sup>;  $\varphi_{\lambda, \text{Fe(II)}}$  is the volume index of refraction of divalent iron in the glass scaled to concentration 10<sup>2</sup> g/cm<sup>3</sup>; it assumes the values 2.25 and 3.60 cm<sup>2</sup>/g at the wavelengths 800 and 1000 nm, respectively.

It follows from the curves presented in Fig. 2 that a systematically higher relative content of Fe<sup>2+</sup> is observed in series LF<sub>2</sub> glasses with higher total iron content. An increase of the phosphorus oxide concentration is accompanied by an increase of the relative Fe<sup>2+</sup> content in glasses from both series,



**Fig. 2.** Relative Fe<sup>2+</sup> content versus the P<sub>2</sub>O<sub>5</sub> amount for series LF<sub>1</sub> (a) and LF<sub>2</sub> (b) glasses.

which on whole agrees with the above-described features of the spectral curves of the model glasses.

It should be noted that the effect of phosphorus oxide on the optical transmission in the visible region at low P<sub>2</sub>O<sub>5</sub> concentrations (0.3% and less) and low content of iron is negligible on the whole. In this connection, the use of small P<sub>2</sub>O<sub>5</sub> additions for doping sheet glass should not greatly de-

grade glass quality with respect to light transmission in the visible region of the spectrum. This effect must be taken into account in glasses with higher iron content. For container glass, where IR transmission is undesirable, the increase of long-wavelength absorption because of the presence of phosphorus can be regarded as a positive phenomenon. This makes it possible to improve the conditions for storing food products.

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